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(54) MULTIPLE OXIDE SINTERED COMPACT AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a sintered compact having high density and good proton conductivity and also to provide its manufacture by which the sintered compact can be manufactured at a lower sintering temp. than the conventional sintering temp.

SOLUTION: This sintered compact is manufactured by adding 0.03 to 1 pts.wt. of at least one oxide selected from oxides of Fe, Co and Ni to 100 pts.wt. of a perovskite multiple oxide represented by the general formula, AB1-xMXO3-a (wherein: A is an element selected from Ca and Sr; B is Zr; M is at least one element selected from Sc, Y, In, Nd, Sm, Gd and Yb; $0<x\leq 0.5$; and $a>0$). At this time, at least one oxide selected from oxides of Fe, Co and Ni, or at least one substance selected from substances which can be converted into these oxides by heating is added to the perovskite multiple oxide and the resulting material is sintered in an oxygen containing atmosphere to manufacture the objective sintered compact.* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1] general formula AB1-X MX O3-a (at least one sort of elements with which A was chosen from calcium and Sr --) B -- Zr -- M -- Sc -- Y -- In -- Nd -- Sm -- Gd -- Yb -- from -- becoming -- a group -- from -- choosing -- having had -- at least -- one -- a sort -- an element -- zero -- < -- X -- <= -- zero . -- five -- a -- > -- zero -- expressing -- having -- perovskite -- a mold -- a multiple oxide -- becoming -- a multiple oxide -- a sintered compact -- setting -- The multiple oxide sintered compact characterized by adding at least one sort of oxides chosen from Fe, Co, and nickel in the range of 0.03 - 1 weight section to the above-mentioned multiple oxide 100 weight section.

[Claim 2] general formula AB1-X MX O3-a (at least one sort of elements with which A was chosen from calcium and Sr --) At least one sort of elements with which B was chosen from the group which consists of Sc, Y, In, Nd, Sm, Gd, and Yb for Zr and M, To the multiple oxide of the perovskite mold expressed with 0< X<=0.5 and a> 0 With at least one sort of oxides or/and heating which were chosen from Fe, Co, and nickel, Above Fe, The mixed process which adds the additive which consists of matter used as at least one sort of oxides chosen from Co and nickel in the range of 0.03 - 1 weight section by these oxides conversion to the above-mentioned multiple oxide 100 weight section, The manufacture

approach of the multiple oxide sintered compact characterized by consisting of a baking process which calcinates the above-mentioned multiple oxide with which the above-mentioned additive was added in an oxygen content ambient atmosphere.

[Claim 3] The burning temperature in the above-mentioned baking process is the manufacture approach of the multiple oxide sintered compact according to claim 2 which is the range of 1200-1500 degrees C.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the sintered compact and its manufacture approach of a multiple oxide of the zirconate system perovskite mold which has proton conductivity.

[0002]

[Description of the Prior Art]

(Outline of a perovskite mold multiple oxide of having proton conductivity), as a

multiple oxide which has proton conductivity, the perovskite mold multiple oxide (A; alkaline earth metal) of the SERETO ($ACeO_3$) system of a lattice defect mold and a zirconate ($AZrO_3$) system etc. is known. It is [that it is easy to react with the carbon dioxide gas in an ambient atmosphere] chemically unstable although a SERETO system has high conductivity. For this reason, the perovskite mold multiple oxide of a zirconate system is having that utilization mainly inquired. In a zirconate system, it is $CaZrO_3$. A system and $SrZrO_3$ There is a system.

[0003] $CaZrO_3$ Or $SrZrO_3$ Although an elevated temperature does not show proton conductivity if it remains as it is, by trivalent metal (M's) ion's permuting tetravalent Zr ion site, and making an oxygen ion hole generate compulsorily comes to show proton conductivity in the ambient atmosphere in which sources of hydrogen, such as hydrogen gas and a steam, exist. Sc, Y, Yb, Nd, Gd, In, etc. are used for the above-mentioned trivalent metal (M). The hydrogen which makes proton conductivity discover is made to introduce into the location near the oxygen ion in an oxide in the form of a proton out of an ambient atmosphere. In this multiple oxide, since hydrogen is not the component which builds the crystal structure, proton conductivity is comparatively acquired by stability to an elevated temperature. The proton which shows conductivity is said to carry out the hopping of between oxygen ion, and to move, making oxygen ion and OH

association in a multiple oxide.

[0004] Generally the multiple oxide of the zirconate system perovskite mold of the above-mentioned lattice defect mold accompanies the electronic conductivity (P-type semiconductor) and oxygen ion conductivity by the electron hole on the defect structure. The amount of protons in a multiple oxide becomes settled in the balance with an ambient atmosphere, and proton conductivity becomes dominant, so that a steam partial pressure is so high that oxygen tension is high and a hydrogen partial pressure is high. Moreover, with lifting of temperature, the amount of dissolutions to the multiple oxide of a proton decreases, and proton conductivity falls. This zirconate system perovskite mold multiple oxide is said for a 400-800-degree C temperature requirement to show the proton conductivity of about ten to 3 S-cm -1 to stability in the hydrogen air current.

[0005] It is CaZr0.9In0.1 O3-a to the typical thing of the multiple oxide of a zirconate system perovskite mold. It is and is already put in practical use as a hydrogen sensor in molten metal. moreover, a steam and NOX CO2 etc. -- it is expected in various fields, such as a solid electrolyte of various gas sensors, a steam electrolytic device, a hydrogen pump, or a fuel cell.

(Reason for the need of a high-density sintered compact)

It is necessary to use this multiple oxide as the highest-density possible sintered compact for the following reasons. That is, in order to raise the inter-electrode gas electric shielding nature prepared the both sides of a substrate, or within and without the Tammann tube in order to reduce electric resistance and to obtain high proton conductivity, raising the dependability on the strength as the structure is called for.

(The conventional means and its trouble for obtaining a high-density sintered compact)

Generally the multiple oxide of the perovskite mold of the zirconate system which has proton conductivity mixes metal carbonate metallurgy group oxide etc. with a ball mill etc. by the predetermined ratio, and after carrying out temporary quenching at the temperature of 900-1400 degrees C in atmospheric air, a ball mill etc. grinds it and it is manufactured. This powder is fabricated in the configuration of a substrate, the Tammann tube, etc., it calcinates at an elevated temperature 1500 degrees C or more among atmospheric air, and the sintered compact of the multiple oxide of the perovskite mold which has proton conductivity is manufactured. Under the present circumstances, in order to make burning temperature high, the expensive electric furnace facility had to be installed, buildup of a manufacturing cost -- power energy increases -- was

imitated, and there was a problem of **. Then, even if it reduced burning temperature, a new means with which a high-density sintered compact is obtained was desired.

[0006] Generally with the ceramics, burning temperature can be reduced by using powder with a particle size small if possible, or adding sintering acid. A means to form a detailed coprecipitation Mr. object in JP,2-293319,A using the solution and the solution for precipitate of mineral salt or organic salt, to carry out temporary quenching of this coprecipitation Mr. object to it, and to obtain detailed multiple oxide powder is indicated. However, in order to obtain a high-density sintered compact, when a high burning temperature of 1500 degrees C was needed too, there was a trouble that a process made it complicated.

[0007] Moreover, it is La 2O3 as sintering acid. SrZrO3 which added Y when it added There is report [THIRD EURO-CERAMICS vol.2(1993) pp.353-358 that a degree of sintering is improved and a precise sintered compact is obtained. Although it seems that a degree of sintering is improved when trivalent La carries out permutation dissolution of this to divalent Sr site where an ionic radius is near, in order to obtain a precise sintered compact, when a high burning temperature of 1600 degrees C is needed, the actual condition is that the effect to proton conductivity is not still sufficiently clear.

(The outline and trouble of an example which add NiO etc. in manufacture of the perovskite mold multiple oxide which has electronic conductivity)

It is La(calcium or Sr) CrO3 as a multiple oxide which, on the other hand, takes the same perovskite type structure, and has electronic conductivity at an elevated temperature. It is known. By permuting a part of trivalent La by divalent calcium or divalent Sr, this multiple oxide changes a part of trivalent Cr into tetravalence, and gives the electronic conductivity by the electron hole as a P-type semiconductor. Consequently, Cr of the transition metals which a valence tends to increase that this multiple oxide tends to oxidize serves as a component of the crystal structure, and differs from the multiple oxide of the perovskite mold of a zirconate system with which not an oxygen ion hole but the point which has introduced valence change of Cr compulsorily has proton conductivity greatly. This multiple oxide is a difficulty sintered material, it is high-density, and since the outstanding sintered compact of electronic conductivity is hard to be obtained, the approach Co, Mn, nickel, etc. of transition metals permute a part of Cr as an improvement means of a degree of sintering is indicated by JP,4-65355,A and JP,4-219364,A. Since a degree of sintering is improved by the above-mentioned approach and a high-density sintered compact is obtained, it is a thing that electronic conductivity improves.

[0008] La(calcium or Sr) CrO3 since it is only a refractory material that a multiple oxide is a difficulty degree of sintering -- not only -- chrome oxide tends to evaporate, and this deposits in the grain boundary, and the atomic diffusion in sintering is checked or it thinks for checking migration dissipation of the pore in a grain boundary. Addition of Co, Mn, nickel, etc. is explained to be what has the effectiveness which promotes lowering, grain boundary diffusion, and volume diffusion in the vapor pressure of chrome oxide. multiple oxide [of the perovskite mold of the zirconate system which has proton conductivity], for example, SrZr0.9 Yb0.1 O3-, a **** -- trivalent Yb ion needs to permute tetravalent Zr ion site in part, and it is necessary to make an oxygen ion hole generate compulsorily Therefore, it consists of an element whose valence was stable, i.e., divalent Sr, tetravalent Zr, and trivalent Yb. Since there was a possibility of permutation dissolution of the Zr ion site where the ionic radius approached having been carried out, having decreased an oxygen ion hole, and reducing proton conductivity, addition of Co, Mn, nickel, etc. which a valence tends to increase that it is easy to oxidize was not considered at all until now.

[0009]

[Problem(s) to be Solved by the Invention]

The object of this invention is to offer the approach of manufacturing the multiple oxide sintered compact and this multiple oxide sintered compact of a zirconate system perovskite mold which have high-density and good proton conductivity with a burning temperature lower than before.

[0010]

[Means for Solving the Problem]

When this invention persons examined various optimal sintering acid to the multiple oxide of the perovskite mold of the zirconate system which has proton conductivity and minute amount addition of at least one sort of oxides chosen from Fe, Co, and nickel was moreover carried out extremely, they found out that a degree of sintering was substantially improvable, without reducing proton conductivity, and resulted in this invention.

[0011] namely, the multiple oxide sintered compact of this invention -- general formula AB1-X MX O3-a (at least one sort of elements with which A was chosen from calcium and Sr --) B -- Zr -- M -- Sc -- Y -- In -- Nd -- Sm -- Gd -- Yb -- from -- becoming -- a herd -- from -- choosing -- having had -- at least -- one -- a sort -- an element -- zero -- < -- X -- <= -- zero . -- five -- a -- > -- zero -- expressing -- having -- perovskite -- a mold -- a multiple oxide -- becoming -- a multiple oxide -- a sintered compact -- setting -- It is characterized by adding at least one sort of

oxides chosen from Fe, Co, and nickel in the range of 0.03 - 1 weight section to this multiple oxide 100 weight section.

[0012] Moreover, the manufacture approach of the multiple oxide sintered compact of this invention general formula AB1-X MX O3-a (at least one sort of elements with which A was chosen from calcium and Sr --) At least one sort of elements with which B was chosen from the group which consists of Sc, Y, In, Nd, Sm, Gd, and Yb for Zr and M, To the multiple oxide of the perovskite mold expressed with 0< X<=0.5 and a> 0 With at least one sort of oxides or/and heating which were chosen from Fe, Co, and nickel, Above Fe, The mixed process which adds the additive which consists of matter used as at least one sort of oxides chosen from Co and nickel in the range of 0.03 - 1 weight section by these oxides conversion to the above-mentioned multiple oxide 100 weight section, It is characterized by consisting of a baking process which calcinates this multiple oxide with which the above-mentioned additive was added in an oxygen content ambient atmosphere.

[0013]

[Embodiment of the Invention]

At least one sort of oxides with which the multiple oxide sintered compact of this invention was chosen as the multiple oxide of a PUROBESU kite mold

from Fe, Co, and nickel are added. The multiple oxide of this invention is the PUROBUSU kite mold which has proton conductivity, and is general formula AB1-X MX O3-a. It is expressed.

[0014] In addition, the inside A of a general formula consists of at least one sort of elements chosen from calcium and Sr, and at least one sort of elements by which B was chosen from the group which Ar and M become from Sc, Y, In, Nd, Sm, Gd, and Yb. Moreover, the range of X is $0< X<=0.5$, and a is $a> 0$. The addition of at least one sort of oxides chosen from Fe, Co, and nickel which are added by the above-mentioned multiple oxide is the range of 0.03 - 1 weight section to this multiple oxide 100 weight section.

[0015] If the consistency of the addition of the above-mentioned oxide of a sintered compact does not improve but it exceeds 1 weight section under in the 0.03 weight section, proton conductivity will fall. It is thought that at least one sort of oxides chosen from Above Fe, Co, and nickel are unevenly distributed in a sintered compact in the grain boundary of the above-mentioned multiple oxide. The oxide of Fe, Co, and nickel may be added with gestalten, such as FeO, Fe 3O4, Fe 3O3, CoO, Co 3O4, and NiO.

[0016] The manufacture approach of the multiple oxide sintered compact of this invention consists of a mixed process which adds the additive which consists of

matter used as at least one sort of oxides chosen from Above Fe, Co, and nickel by at least one sort of oxides or/and heating which were chosen as the multiple oxide of a perovskite mold from Fe, Co, and nickel, and a baking process which calcinates this multiple oxide with which the above-mentioned additive was added in an oxygen content ambient atmosphere.

[0017] The additive which consists of matter used as at least one sort of oxides chosen from Above Fe, Ci, and nickel by at least one sort of oxides or/and heating which were chosen from Fe, Co, and nickel which are added by the above-mentioned multiple oxide is added in the range of 0.03 - 1 weight section to this multiple oxide 100 weight section. Since the reduction effectiveness of burning temperature, i.e., the improvement effect of a degree of sintering, will not be enough acquired if the addition of the above-mentioned additive added by this multiple oxide becomes under the 0.03 weight section, it is not desirable. Moreover, even if an addition makes [many] it exceeding 1 weight section, since about [that the improvement effect of a degree of sintering is not acquired more than it] and proton conductivity falls, it is not desirable.

[0018] In addition, as an oxide of Fe, Co, and nickel, FeO, Fe 3O4, Fe 2O3, CoO, Co 3O4, NiO, etc. can be used. Moreover, heating may decompose and the oxide of Fe, Co, and nickel may turn into an oxide. For this reason, the organic

compound and hydroxide containing Fe, Co, and nickel, a carbonate, a nitrate, an oxalate, acetate, etc. can use it as matter which serves as an oxide of Fe, Co, and nickel with heating.

[0019] Here, let the addition of the matter used as at least one sort of oxides chosen from Above Fe, Co, and nickel by heating be the range of 0.03 - 1 weight section to the multiple oxide 100 weight section by these oxides conversion. In this case, since there is an oxide of various valences, the addition of the matter which serves as the above-mentioned oxide with heating on the basis of the oxide usually formed on the baking conditions in a baking process is determined as at least one sort of oxides chosen from Fe, Co, and nickel.

[0020] For example, when using the oxalate of Fe as matter which serves as the above-mentioned oxide with heating, since the oxide usually formed on the baking conditions in a baking process is FeO, FeO determines in this case that the addition of the oxalate of Fe will become 0.03 - 1 weight section to the multiple oxide 100 weight section. The perovskite mold multiple oxide powder of the zirconate system which has proton conductivity mixes metal carbonate metallurgy group oxide etc. with a ball mill etc. by the predetermined ratio beforehand, and among atmospheric air, at the temperature of 900-1400 degrees C, temporary quenching of it is carried out and it is prepared. That is, it

is necessary to consider as the perovskite mold multiple oxide of a zirconate system beforehand. If additives, such as at least one sort of oxide chosen as the raw material of a PUROBUSU kite mold multiple oxide from Fe, Co, and nickel, are added and a PUROBUSU kite mold multiple oxide is formed, the properties of a PUROBUSU kite mold multiple oxide, such as proton conductivity, will fall. This is general formula AB1-X MX O3-a of a PUROBUSU kite mold multiple oxide by operation of the above-mentioned additive. It thinks because M stops being able to dissolve easily in the location of B. In addition, especially the formation approach of this multiple oxide is not limited. For example, a coprecipitate is produced with the coprecipitation method [raw material / predetermined] using a nitrate etc., temporary quenching of this may be carried out and it may be obtained. The additive which consists of matter which serves as the above-mentioned oxide with at least one sort of oxide or/and heating which were chosen from Fe, Co, and nickel is added by temporary-quenching powder with grinding by a ball mill etc. Since it is mixable into temporary-quenching powder at homogeneity even if it is minute amount addition if grinding processing is carried out beforehand, it is desirable. Moreover, in order to raise a degree of sintering further, you may add into the temporary-quenching powder ground beforehand.

[0021] In this way, the perovskite mold multiple oxide powder of the zirconate system which has the acquired proton conductivity is fabricated by the configuration of a substrate, the Tammann tube, etc., and is calcinated in the oxygen content ambient atmosphere of the atmospheric-air middle class. N2 In the ambient atmosphere in which oxygen, such as Ar, is not contained, an operation of the above-mentioned additive is hard to be demonstrated, and the improvement effect of a degree of sintering is not acquired enough. Although burning temperature changes also with the classes and additions of sintering acid, the range of it is about 1200-1500 degrees C. If it calcinates at temperature lower than 1200 degrees C, a high-density sintered compact will be hard to be obtained. Moreover, if it calcinates at temperature higher than 1500 degrees C, although a high-density sintered compact will be obtained compared with the sintered compact which is not added [usual], the object of making burning temperature low is not met. Heating time is 1 - 12 hours in general. The shorter one is desirable if the power energy cost which heating takes is taken into consideration.

[0022]

[Example]

Hereafter, an example explains to a detail further.

(Example 1) $SrCO_3$ with a mean particle diameter of 2 micrometers and ZrO_2 with a mean particle diameter of 4 micrometers And Yb_2O_3 with a mean particle diameter of 3 micrometers It mixes by the predetermined ratio, and among atmospheric air, temporary quenching is carried out for 10 hours, and it grinds at 1350 degrees C, and is $SrZr_{0.9}Yb_{0.1}O_{3-a}$. Multiple oxide powder with a mean particle diameter of 0.6 micrometers was produced by the presentation. a is calculated with 0.05 here. Similarly, they are $SrCO_3$ with a mean particle diameter of 2 micrometers and ZrO_2 of 4 micrometers of average grains. And In_2O_3 with a mean particle diameter of 3 micrometers It mixes by the predetermined ratio, and among atmospheric air, temporary quenching is carried out for 10 hours, and it grinds at 1350 degrees C, and is $CaZr_{0.9}In_{0.1}O_{3-a}$. Multiple oxide powder with a mean particle diameter of 0.6 micrometers was produced by the presentation. a is calculated with 0.05 here.

[0023] One weight section addition of the thing of only two sorts of above-mentioned multiple oxide powder and the various transition-metals oxide shown in a table 1 at the multiple oxide powder 100 weight section was carried out, and preferential grinding was carried out with a wet one with the ball mill for 24 hours, and it dried after that and considered as powder. It is atmospheric air,

and Ar and N2 about the ambient atmosphere at the time of baking after fabricating this mixed powder disc-like. It changed and calcinated at the temperature of 1250 degrees C for 4 hours. The result of having investigated the relative density of each sintered compact was shown according to a table 1. In addition, La 2O3 Although it added similarly even if attached, it is the shaping back La 2O3. CO2 in air Since it absorbed and the produced Plastic solid became scattering, baking was stopped.

[0024] SrZr0.9 Yb0.1 O3-a A presentation and CaZr0.9 In0.1 O3-a With both the multiple oxide powder of a presentation, when the oxide of Fe, Co, and nickel was added and it moreover calcinated in atmospheric air, the sintered compact with a high consistency was obtained. When especially the oxide of Co and nickel was added, the consistency became 95% or more and the remarkable degree-of-sintering improvement effect was shown. For example, in No.8 and No.17, 98% or more of high-density sintered compact was obtained by addition of NiO even in a low burning temperature of 1250 degrees C among atmospheric air. On the other hand, in the thing pan which added transition-metals oxides other than a non-added thing and Fe and Co, and nickel (namely, oxide of Ti, V, Cr, Mn, and Cu), it is Ar or N2. It is 80% or less which was sintered under gas, and its a consistency is inadequate for the object of

densification.

[0025]

[A table 1]

試料番号	複合酸化物種類	遷移金属酸化物の種類	焼成雰囲気	焼結体相密度(%)
1*	$SrZr_{0.9}Yb_{0.1}O_{3-a}$	未添加	大気	78.6
2*	〃	TiO_2	〃	77.8
3*	〃	V_2O_3	〃	79.0
4*	〃	Cr_2O_3	〃	78.2
5*	〃	Mn_2O_3	〃	79.5
6	〃	Fe_3O_4	〃	87.3
7	〃	Co_3O_4	〃	95.0
8	〃	NiO	〃	98.9
9*	〃	CuO	〃	79.8
10*	$CaZr_{0.9}Yb_{0.1}O_{3-a}$	未添加	〃	79.0
11*	〃	TiO_2	〃	78.0
12*	〃	V_2O_3	〃	79.2
13*	〃	Cr_2O_3	〃	78.5
14*	〃	Mn_2O_3	〃	79.3
15	〃	Fe_3O_4	〃	88.8
16	〃	Co_3O_4	〃	96.2
17	〃	NiO	〃	99.3
18*	〃	CuO	〃	78.6
19*	$SrZr_{0.9}Yb_{0.1}O_{3-a}$	未添加	Ar	73.8
20*	〃	Fe_3O_4	〃	73.0
21*	〃	Co_3O_4	〃	73.4
22*	〃	NiO	〃	76.7
23*	〃	NiO	N_2	77.0

*; it is SrZr0.9 Yb0.1 O3-a like the example 1 which shows the example of a comparison (example 2). The NiO addition was changed into the multiple oxide powder of a presentation in the range of 0 - 3 weight section, and the relation

between the burning temperature in atmospheric air and the relative density of the obtained sintered compact was investigated. A result is shown in a table 2. The holding time of baking presupposed that it is fixed for 4 hours.

[0026] Burning temperature compared on the same conditions and the relative density of a sintered compact increased from the NiO case of not adding, clearly by addition of NiO. By adding NiO and choosing burning temperature appropriately in 1200-1500 degrees C showed that the high-density sintered compact of 98% or more of relative density was obtained. If an addition becomes less than the 0.03 weight section, the reduction effectiveness of burning temperature, i.e., the improvement effect of a degree of sintering, will not be acquired enough. Moreover, more than it, even if it adds more mostly than 1 weight section, as the improvement effect of a degree of sintering is not acquired but assessment of an example 3 shows, proton conductivity falls.

[0027]

[A table 2]

試料番号	NiO 添加量(WT%)	焼成温度（℃）	焼結体相対密度（%）
2 4*	未添加	1050	66.8
2 5*	〃	1150	71.5
2 6*	〃	1250	78.6
2 7*	〃	1350	86.3
2 8*	〃	1450	94.7
2 9*	〃	1550	98.0
3 0*	〃	1650	98.9
3 1	0.03	1050	68.0
3 2	〃	1150	76.8
3 3	〃	1250	85.3
3 4	〃	1350	93.6
3 5	〃	1450	98.4
3 6	0.06	1050	70.8
3 7	〃	1150	79.7
3 8	〃	1250	89.5
3 9	〃	1350	98.0
4 0	〃	1450	98.5
4 1	0.15	1050	74.0
4 2	〃	1150	83.4
4 3	〃	1250	93.5
4 4	〃	1350	99.0
4 5	〃	1450	99.9
4 6	0.3	1050	79.8
4 7	〃	1150	89.0
4 8	〃	1250	98.2
4 9	〃	1350	99.5
5 0	〃	1450	99.3
5 1	1.0	1050	82.1
5 2	〃	1150	91.0
5 3	〃	1250	99.0
5 4	〃	1350	98.9
5 5	〃	1450	98.5
5 6*	2.0	1050	82.0
5 7*	〃	1150	91.2
5 8*	〃	1250	99.0
5 9*	〃	1350	98.8
6 0*	〃	1450	98.1
6 1*	3.0	1050	82.1
6 2*	〃	1150	91.1
6 3*	〃	1250	99.1
6 4*	〃	1350	98.6
6 5*	〃	1450	97.7

*; using the sintered compact (sample number 48) which carried out 0.3 weight section addition of the NiO among the samples produced in the example 2 which shows the example of a comparison (example 3), and was produced at the temperature of 1250 degrees C, the hydrogen concentration cell was constituted and the electromotive force was investigated. The grinding process of the sintered compact 1 was first carried out to 0.6mm in thickness, and the Pt electrode 2 with a thickness of 1000A was formed in the both sides of a sintered compact 1 using ion coater. When it installed in the hydrogen concentration cell of a configuration of that this is shown in drawing 1 , and H2 / Ar was made the negative electrode, 98 ml/min style of H2 / the Ar was made to 34 ml/min sink and the positive electrode 0.1% 3% and the electromotive force in 400-800 degrees C was measured, the theoretical electromotive force expressed with formula E=RT / 2FLnPH2 / P'H2 of Nernst was acquired. The transference number of a proton is about 1 and it has checked having proton conductivity.

[0028] Then, the steam electrolytic device shown in drawing 2 was constituted using the high density sintered compact of 98% or more of relative density produced in the example 2, and the relation between a NiO addition and a steam electrolysis property was investigated. The grinding process of each sintered

compact 1 was similarly carried out to 0.6mm in thickness, and the Pt electrode 2 with a thickness of 1000A was formed in the both sides of a sintered compact 1 using ion coater. This was installed in the steam electrolytic device of a configuration of being shown in drawing 2 , and the whole was heated at 480 degrees C at the external heater (not shown). 100%H2 O is turned on an anode side, 30 ml/min style of the pure Ar is carried out to a 400 ml/min sink cathode side, and they are 4 mA/cm2 to inter-electrode. The fixed current was passed. It is H2 by the gas-chromatograph monitor installed in the lower stream of a river by the side of a cathode. When the yield was investigated and the electrolysis effectiveness was searched for, the result of a table 3 was obtained.

[0029] By the sample below 1 weight section, the addition of NiO showed the value with almost fixed electrolysis effectiveness as about 27%. That is, the sintered compact which added NiO was also found by that the same steam electrolysis property as a non-added thing is acquired when the addition was below 1 weight section. Minute amount addition of NiO is SrZr0.9 Yb0.1 O3-a, as a result of increasing the lattice defect in a grain boundary or a grain in a sintering process and promoting grain boundary diffusion or volume diffusion. What improves a degree of sintering remarkably is presumed. Since it is minute amount addition, it is thought that proton conductivity was not spoiled.

[0030] Moreover, in the added sintered compact, electrolysis effectiveness fell with the addition. NiO added superfluously is presumed to be that to which electrolysis effectiveness fell, as a result of not approving in buildup of a lattice defect, segregating a degree of sintering to about [that the effectiveness improved more than it is not acquired] and reverse in the grain boundary of a sintered compact and checking proton conductivity. Moreover, the high-density sintered compact which has good proton conductivity extremely when the addition found out that an improvement effect large in a minute amount was acquired can produce now easily by specifying the oxide sintering acid which improves a degree of sintering with a burning temperature lower [100 degrees C of numbers] than before.

[0031]

[A table 3]

試料番号	N i O添加量 (w t %)	焼成温度 (℃)	相対密度 (%)	水蒸気電解効率 (%)
2 9*	未添加	1550	98.0	27.0
3 5	0.03	1450	98.4	27.1
3 9	0.06	1350	98.0	26.8
4 4	0.15	1250	98.0	27.2
4 8	0.3	1250	98.2	27.0
5 3	1.0	1250	99.0	26.8
5 8*	2.0	1250	99.0	23.5
6 3*	3.0	1250	99.1	13.6

*; [0032] which shows the example of a comparison

[Effect of the Invention]

As explained above, since at least one sort of oxides with which the multiple oxide sintered compact of this invention was chosen from Fe, Co, and nickel as the multiple oxide of the PUROBUSU kite mold of the zirconate system which has proton conductivity are added, the consistency of a sintered compact is high and proton conductivity will become good.

[0033] According to the manufacture approach of the multiple oxide of this invention, moreover minute amount addition is carried out extremely, and the additive which consists of matter used as at least one sort of oxides chosen from Above Fe, Co, and nickel by at least one sort of oxides or/and heating which were chosen from Fe, Co, and nickel as the multiple oxide of the perovskite mold of the zirconate system which has proton conductivity is calcinated in an oxygen content ambient atmosphere. For this reason, in a burning temperature of 1200-1500 degrees C lower hundreds of degrees C than before, gas electric shielding nature is high and, easy moreover, the perovskite mold multiple oxide sintered compact of the zirconate system which has high-density and good proton conductivity with high dependability on the strength is obtained with

sufficient repeatability.

[0034] If the above-mentioned additive is added to the multiple oxide of a perovskite mold, in order that at least one sort of oxide chosen from Fe, Co, and nickel from this additive may be unevenly distributed in the grain boundary of the multiple oxide of a PUROBUSU kite mold and may promote grain boundary diffusion and volume diffusion, it will be thought that a degree of sintering is improved substantially. In addition, the matter used as at least one sort of oxides chosen from Fe, Co, and nickel by heating and the becoming matter change to the oxide chosen from Fe, Co, and nickel by heating at the time of baking. And since a high-density sintered compact is extremely obtained by addition of a minute amount, proton conductivity is not spoiled.

[0035] As a result, gas electric shielding nature is high and can manufacture the multiple oxide sintered compact of the zirconate system perovskite mold which has high-density and good proton conductivity with high dependability on the strength with a burning temperature lower than before.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the configuration schematic diagram of the hydrogen

concentration cell used in the example.

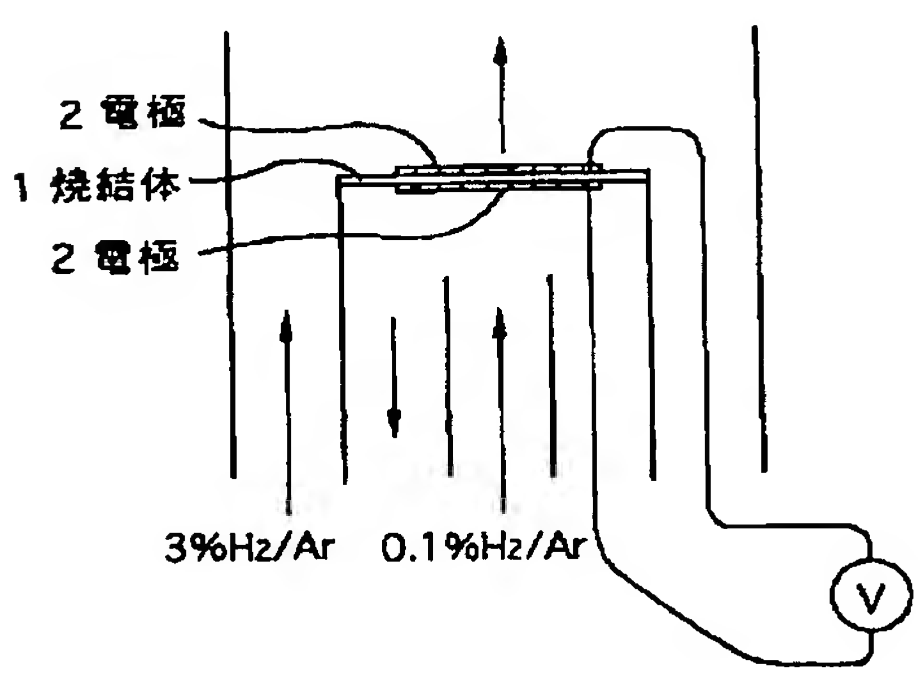
[Drawing 2] It is the configuration schematic diagram of the steam electrolytic device used in the example.

[Description of Notations]

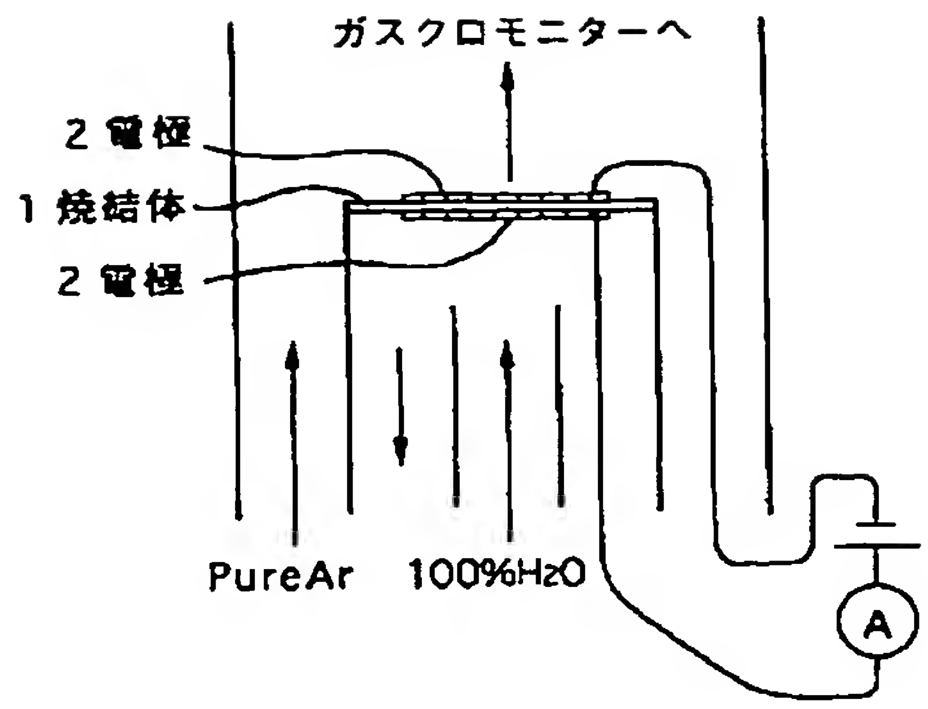
1: Sintered compact 2: Electrode

DRAWINGS

[Drawing 1]



[Drawing 2]


ガスクロモニターへ
2 電極
1 焼結体
2 電極
PureAr
100%H2O
A